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OPHTHALMOLOGIC GLASS WITH ENHANCED REFRACTIVE INDEX

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Glasses with refractive index 1.60 – 1.65, density 2.80 – 3.08 g/cm^3 and dispersion coefficient ≥ 45 have been developed on the basis of the system $Na_2O(K_2O)$–MgO–CaO–BaO–ZnO–B_2O_3–SiO_2. These glasses are recommended for use in ophthalmologic lenses.

Key words: optical glass, ophthalmologic optics, refractive index, density, dispersion coefficient.

Organic materials are finding more and more applications in the manufacture of ophthalmologic lenses. The advantage of these materials is their density, which is much lower than that of silicate glass. Correspondingly, the mass of a lens made from organic material with the same optical properties is significantly lower. Optical glass as a material for ophthalmologic lenses can be made more competitive by decreasing the thickness of ophthalmologic lenses, which is possible for optical glass with a high refractive index. In this connection the manufacturers of ophthalmologic lenses use high-index glasses, whose refractive index exceeds 1.60. However, the advantages of high-index glasses can be realized only with relatively low glass density. The dispersion coefficient (Abbe number) is also important: the higher its value, the smaller the chromatic aberration of a lens [1].

In summary, the glasses used to manufacture ophthalmologic lenses must satisfy a set of properties: the refractive index must be high, the dispersion coefficient large and the density low. In addition, they must possess sufficient hardness and low transmission coefficient for ultraviolet and infrared radiation and be chemically stable with respect to a humid atmosphere and staining agents.

The refractive index of the BOK-3 glass now used at the Zavod Optik, JSC (Lida, Republic of Belarus), for ophthalmologic lenses is $n_e = 1.525$, the Abbe number 58.3 and density 2.53 g/cm^3. In terms of its refractive index this glass is medium-index glass. OST 3-465–84 regulates BOF-60 and BOF-65 glasses, whose refractive indices are 1.6095 and 1.6530. A drawback of these glasses is their density, equal to 3.16 and 3.37 g/cm^3, respectively, as well as the presence of lead oxide — a class-1 hazard — in their recipe.

According to GOST 3514–94, optical glasses with refractive index $n_e = 1.60 – 1.65$ can be used for manufacturing ophthalmologic lenses. These glasses are of the following types: TK — heavy crown, F — flints, and BF — barytic flints. The main characteristics of these glasses are presented in Table 1.

Glasses of the types F1, F6 and F9 are obtained on the basis of the system K_2O–PbO–SiO_2 with lead oxide content 17 – 22 mol.%[3] [2]. With refractive indices 1.6070 – 1.6180 these glasses are characterized by low dispersion coefficients and high density, which is due to a significant molar content of lead oxide (to 19 – 35%). The F9 glass has a lower density, comprising 2.93 g/cm^3. However, it contains a fluorine compound (F^- content 18.44%).

The barytic flints were obtained on the basis of the system K_2O–BaO–ZnO–PbO–SiO_2 with additions of Na_2O, CaO and B_2O_3. They are characterized by high dispersion coefficients, but their density is less than 3.47 g/cm^3 and increases with increasing refractive index.

The heavy crown glasses are synthesized in the system BaO–B_2O_3–SiO_2 with 34.0 – 58.7 % SiO_2 and to 31.8 % BaO. In addition, Na_2O, K_2O, ZnO and Al_2O_3 can be added in TK glasses. The dispersion coefficient of heavy crown glasses, indicated in Table 1, lies in the range 54.83 – 60.39 with refractive index ≥ 1.6063. However, because of the elevated barium oxide content these glasses have high refractive indices.

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[3] Here and below the molar content, mol.%, unless otherwise stipulated.

TABLE 1. Main Characteristics of Glasses with Refractive Index 1.60 – 1.65

Glass type	n_e	ν_e	Density, g/cm^3	Glass type	n_e	ν_e	Density, g/cm^3
TK4	1.6138	55.55	3.58	F1	1.6169	36.70	3.57
TK8	1.6168	54.83	3.61	F6	1.6070	37.68	3.48
TK13	1.6063	60.39	3.44	F9	1.6180	34.31	2.93
TK14	1.6155	60.34	3.51	BF11	1.6251	52.84	3.66
TK16	1.6152	58.09	3.56	BF12	1.6298	38.43	3.67
TK17	1.6305	59.09	3.66	BF21	1.6178	39.76	3.56
TK20	1.6247	56.43	3.58	BF25	1.6108	45.82	3.47

In summary, brand name optical glasses do not meet a set of conditions imposed on the glasses used in ophthalmologic lenses. For this reason the problem of obtaining glass with refractive index ≥ 1.60 and density ≤ 3.0 g/cm^2 was posed. For this it was also necessary to secure the required technological properties: no crystallization during the formation of articles and low aggressiveness of the molten glass. Economics is also important, since rare-earth oxides, specifically, lanthanum oxide, an expensive material, are widely used in the development of high-index optical glasses. In addition, it is undesirable to use class-1 hazard components, specifically, lead compounds.

The multicomponent system Na_2O–*R*O–B_2O_3–SiO_2, where *R*O = MgO, CaO, ZnO, SrO and BaO, was chosen as the base for synthesizing the glasses. The effect of the components on the glass density was taken into account in picking the glass compositions, so that calcium oxide, which is introduced into the experimental glasses in amounts to 20%, was chosen as the main *R*O-group oxide. The base composition of the glass includes the following (mol.%): 10 Na_2O, 20 CaO, 5 B_2O_3 and 65 SiO_2.

The glasses were made in a gas flame furnace at temperature 1400 – 1450°C in porcelain and corundum crucibles.

Glass with the base composition is characterized with the refractive index 1.5493 and density 2.518 g/cm^3. To increase the refractive index and improve the technological properties of the synthesized glasses two or more *R*O-group components in different ratios were introduced into the base composition by replacing some SiO_2 with the oxides BaO, ZnO, SrO and MgO. The content of the components was varied in the following limits (%): BaO — from 1 to 20; ZnO — from 5 to 12; SrO — from 2 to 6; and, MgO — from 2 to 6.

The results of the determination of the refractive index of the glasses by the immersion method and the density of the experimental glasses, which are characterized by the best technological properties, are presented in Fig. 1.

It was determined that the refractive index can be increased most effectively by introducing CaO and BaO simultaneously. However, when the refractive index reaches 1.60 the glass density surpasses 3.1 g/cm^3.

When barium and zinc oxides are introduced in the ratio 1 : 4, magnesium, barium and zinc oxides in the ratios 1 : 1 : 2 and magnesium, strontium, barium and zinc oxides in the ratios 2 : 2 : 1 : 5 the refractive index increases less than when BaO alone is introduced, but the experimental glass density does not increase as much. Magnesium oxide is effective, but its content cannot exceed 4% because heat treatment increases the crystallization power of the glasses.

Introduction of the oxides CaO, ZnO, MgO, SrO and BaO simultaneously lowers the crystallization power, which is manifested during gradient heat-treatment by the formation of a crystalline film in the temperature interval 700 – 950°C. Glass-forming melts do not manifest aggressiveness toward the material of the porcelain crucibles used for glass melting.

To obtain enhanced-index glass the sodium oxide in experimental glass compositions with MgO : SrO : BaO : ZnO = 2 : 2 : 1 : 5 was replaced with potassium and lithium oxides (Fig. 2).

It was found that the introduction of Li_2O not only increases the refractive index of the glasses; it also decreases their density. The melting temperature of the lithium-containing glasses is 1350 ± 20°C. The crystallization power of the experimental glasses increases with increasing Li_2O con-

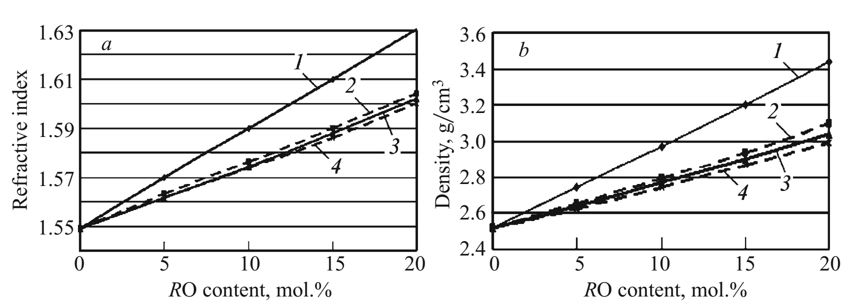

Fig. 1. Effect of *R*O-group oxides on the refractive index (*a*) and density (*b*). Components and their molar ratio: *1*) BaO; *2*) BaO : ZnO = 1 : 4; *3*) MgO : BaO : ZnO = 1 : 1 : 2; *4*) MgO : SrO : BaO : ZnO = 2 : 2 : 1 : 5.

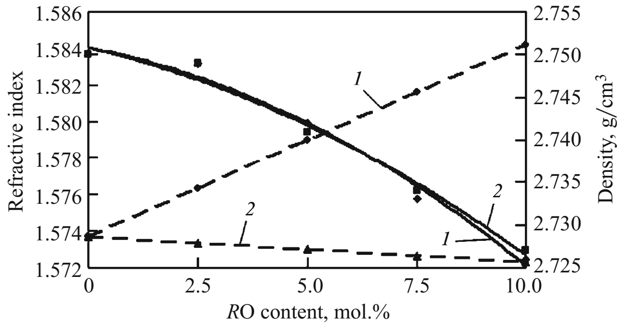

Fig. 2. Effect of R_2O group oxides on the refractive index and density of the experimental glasses: ——) density; – – –) refractive index; *1*) Li_2O; *2*) K_2O.

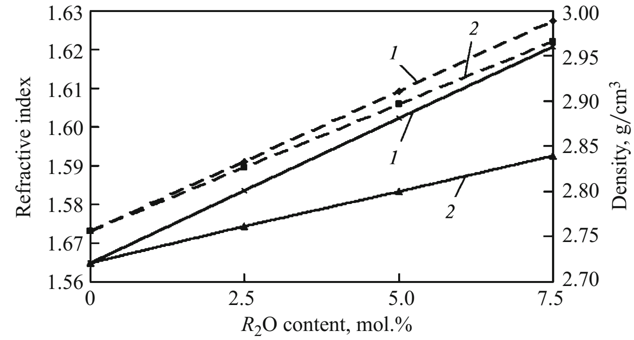

Fig. 3. Effect of TiO_2 and ZrO_2 on the refractive index and density of the experimental glasses: ——) density, – – –) refractive index; *1*) Zr_2O; *2*) TiO_2.

tent, and as a result its content must not exceed 5 – 8%. The low viscosity of the glass melt makes the glass more aggressive than sodium-containing glass, which in the case of commercial synthesis requires refractories with high glass resistance to be used. The introduction of lithium oxide could be desirable only for synthesizing glass with refractive index of the order of 1.65 and higher.

The introduction of 10% K_2O as a replacement for Na_2O lowers the refractive index by 0.015, and the density decreases by 0.023 g/cm^3 at the same time. Varying the content of these components by means of RO-group oxides showed that the optimal amount of K_2O is 5 – 10%.

Since refractive indices corresponding to high-index glass were not reached by varying the content of RO- and R_2O-group oxides, at the next step of this work the glasses were modified by additions of titanium and zirconium oxides, introduced as replacements for SiO_2 in amounts to 7.5% (Fig. 3).

As noted in [3], to devise optical glass composition lead, titanium and lanthanum oxides are widely used as components making it possible to increase the refractive index considerably, while TiO_2 increases glass density much less.

The refractive index of the experimental glasses can be increased to 1.60 and higher by introducing 4 – 7.5% titanium oxide. Technological glasses with refractive index ≥ 1.605 and density 2.8 g/cm^3 were obtained by using TiO_2. The TiO_2 content is capped at 5% because at higher values the experimental glasses acquire a light-yellow hue.

Optimizing the ratio of SiO_2 and RO-group oxides and introducing titanium and zirconium oxides simultaneously in the ratio 2 : 1 gave glass based on the system $Na_2O(K_2O)$–MgO–CaO–BaO–ZnO–B_2O_3–SiO_2 with refractive index 1.65 and density 3.08 g/cm^3.

In summary, it was established that glasses with refractive index 1.60 – 1.65 and density 2.80 – 3.08 g/cm^3 can be obtained on the basis of the system $Na_2O(K_2O)$–RO–B_2O_3–SiO_2 with calcium, zinc and barium oxides introduced simultaneously. The dispersion coefficient of the glasses obtained is at least 45. These glasses are intended for use in the production of ophthalmologic lenses.

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